IDENTIFYING THE NON-POINT SOURCES OF PERFLUORINATED COMPOUNDS USING GEOGRAPHIC INFORMATION SYSTEM (GIS)

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Abstract
Perfluorinated Compounds (PFCs) have recently been detected in a wide range of places. This study examined contribution of the non-point source (NPS) to PFCs in rivers. NPS contribution of PFCs has not been focused much so far. In this study, samples of river water were collected from Tsurumi River at a fixed location during low and high levels of river flow (due to rainfall) and their concentrations of PFCs were analyzed. The loading of PFC congeners increased with the flow rate of river water. This finding showed that NPS contribution existed for some PFCs. Also, source identification was attempted using Geographic Information System (GIS). This technique was used to relate land use of watershed to PFC pollution. The results indicated the relationship between PFC concentrations and commercial or transportation land use. It can be concluded that PFCs have NPS and these are related to land use such as commercial or transportation land use.

Introduction
The pollution by perfluorinated compounds (PFCs) has recently been found to be ubiquitous. PFCs are also accumulated in wildlife in the Arctica[1]. Many researchers mainly considered the volatility of those precursors to be the cause of widespread and ubiquitous contamination[2-4]. However, we speculate that other causes may also be contributory for such widespread contamination. The materials with PFCs are used everywhere including outdoors, because of their brilliant chemical properties including both lipophobic and hydrophobic characteristics. They are used in waterproof agent, rainproof coat, firefighting form, coating painting and are washed out by rain. So they can be non-point sources (NPS). No reports, however, have focused on NPS type pollution phenomena of PFCs.
In this study, we investigated the NPS type characteristic of PFC pollution by sampling the river water during raining periods, and tried to find factors that contributes to such NPS type pollution by using Geographical Information System (GIS). The steps of the current study are described below.

Step 1: Remote sensing with GIS.
Step 2: Determining the sampling sites.
Step 3: Monitoring the river water.
Step 4: NPS identification by using GIS and statistical analysis.

We measured many congeners of PFCs in river water. In recent studies, the GIS was used to identify the NPS of nutrient salts[5] or heavy metal[6]. Hence, we used this system as screening techniques of NPS identification of PFCs. Using such technique (GIS), we tried to explore the existence of the NPS of PFCs and the identification of their sources.

Materials and Methods
Study area and sampling: Study was carried out in Tsurumi River and its tributary, Hayabuchi River in Yokohama, Japan (Fig. 1). The observation point was fixed at Nippa Bridge on Tsurumi River. The samples of river water were collected at this point during April 3, 2006 and May 29, 2006.

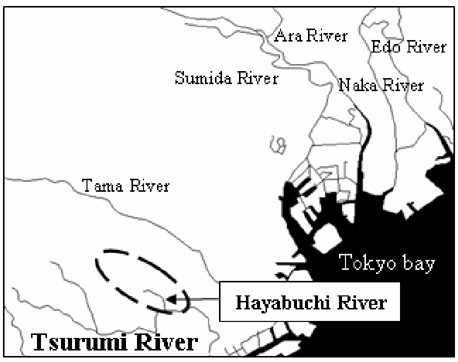

Fig. 1 Study Area

In Hayabuchi River, samples were collected throughout the river stretch on January 9, 2006. On the sampling day, the weather was fine and no rain was observed for the proceeding 2 days. The sewer system in Hayabuchi River basin is separated sewerage, and no wastewater treatment plant exists.

Additionally, coverage of the sewer system is 99.6% in Yokohama. So, in this basin, no sewer water inflows into the river. Rain water drainages, however, are connected to the river. The rain water flows into the river through each storm drain. In this basin, 14 drainages exist and we studied the largest 12 drainages throughout the river stretch.
The water samples were collected in each sampling station using a stainless steel bucket and stored in polypropylene containers. Then the samples were transported to the laboratory with ice bags, and refrigerated at 2 ˚C until analysis.

Chemical Analysis: PFCs were analyzed based on the methods described in the literature[7]. The river water was extracted using Oasis HLB extraction cartridges (500mg/6cc) (Waters, Milford, MA). One liter of water sample was loaded onto the cartridge by Sep-Pak concentrator (Waters, Milford, MA) after elimination of particular matter with glass fiber filter (φ 47 mm, pore diameter 1 μm). And target fraction was eluted with 7 mL of methanol. The eluate was dried under a gentle stream of high-purity nitrogen gas, and resolved with 1 mL of methanol for HPLC-MS/MS analysis. HPLC-MS/MS measurement was performed using an Agilent 1100 high-performance liquid chromatograph (Agilent, Palo Alto, CA) interfaced with a Micromass Quattro tandem mass spectrometer (Waters, Milford, MA) operated in the electrospray negative ion mode. A 10 μL aliquot of extract was injected onto a Zorbax Eclipse XDB C18 column (2.1 mm i.d. × 150 mm length, 5 μm).

We have measured perfluoropentanoate (PFPeA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorobutanesulfonate (PFBS), perfluorohexanesulfonate (PFHxS), perfluorooctanesulfonate (PFOS), perfluorodecanesulfonate (PFDS), isomers of perfluoro-octanesulfonate (isoPFOS), 1H, 1H, 2H, 2H-tetrahydroperfluorooctanesulfonate (THPFOS) in river water. And these chemicals were used as external standards. Only THPFOS came under the severe influence of sample matrix. So, the result of THPFOS was not used.

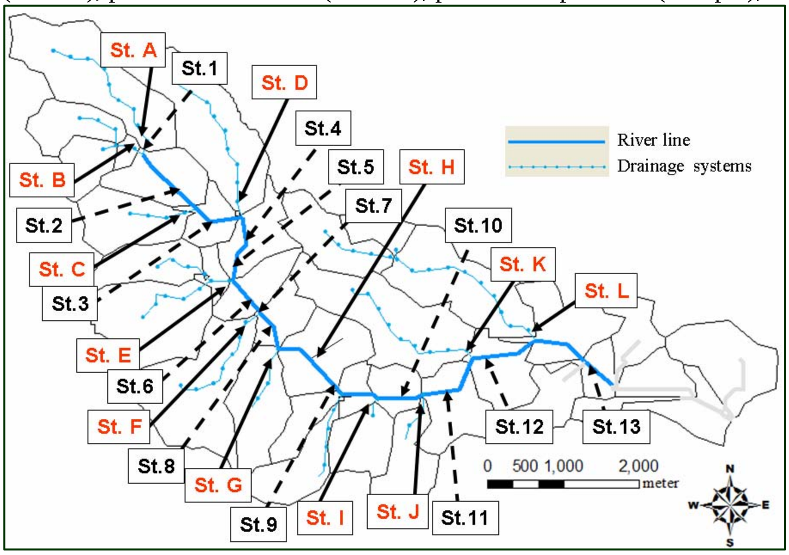

Fig. 2 Sampling site map

It is noted that the resolution (Rs) of isoPFOS and PFOS peaks is calculated to be 0.76.

Analysis using GIS: ArcGIS (ESRI, Inc.) was used for geographical analysis. The watershed map of Hayabuchi River was made from Digital Elevation Model (DEM) data of 50 m mesh. Then the watershed of drainages was re-created. And the data of population and land use were overlapped as layers, and these layers were intersected with watershed layer. The constructed watershed by GIS and sampling site was shown in Fig 2. The sampling points in the Hayabuchi River and those in drainage are shown by NUMBERs and ALPHABETs, respectively.
Although the drainage at St.H was not drawn from DEM data, it exists in actuality. And the simulated drainage from DEM data, situated between St. 9 and St. I could not be found in the field survey. This map, however, reflects the real situation of the Hayabuchi River basin very well as a whole.

NPS analysis: The procedure of the NPS identification method which was applied to Hayabuchi River monitoring is shown in Fig. 3. This study is mainly consisted of two methods; river monitoring and remote sensing with GIS. The sampling sites were determined by GIS analysis. Then the river monitoring was conducted and the concentration of PFCs in water was analyzed. Finally, the source (NPS) identification of PFCs was conducted from the result of river monitoring and GIS analysis.

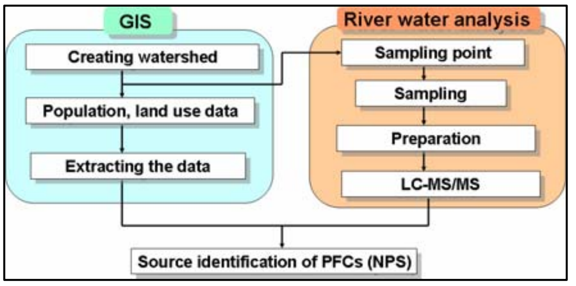

Fig. 3 Research procedure

Results and Discussion

Existence of NPS: The results of the fixed-point sampling at Nippa Bridge in Tsurumi River are shown in Fig. 4 and 5.

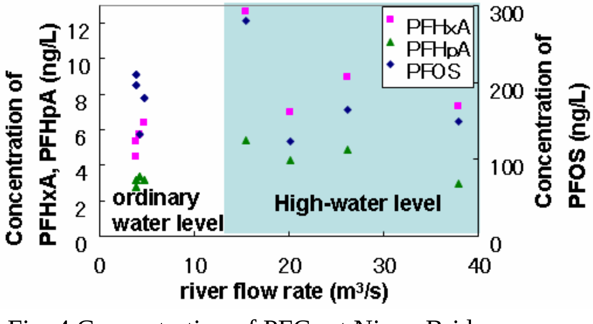

Fig. 4 Concentration of PFCs at Nippa Bridge.

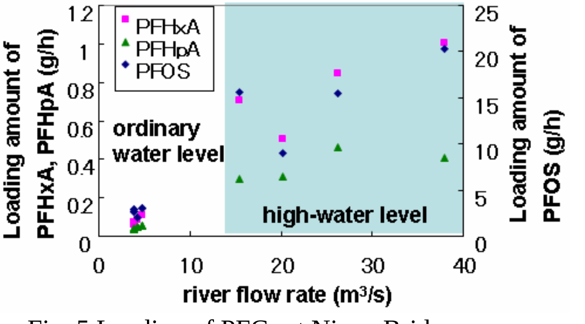

Fig. 5 Loading of PFCs at Nippa Bridge

The concentration levels of PFCs at high river flow were almost the same or a little higher compared with those in ordinary flow (Fig. 4). The loading of PFCs increased with the increase of river water flow. The rain water itself, however, did not contain significant level of PFCs[8]. So, the result means that runoff water contains large amounts of PFCs, probably by eluting PFCs from road, building, or vehicles, indicating that NPS of PFCs existed. Based on these results, we tried to idintify what are the contributing factors to the NPS of PFCs. So a detailed study of the entire river stretch was conducted by using GIS technique (Fig. 3).

Identifying PFC Sources with GIS: To research the sources of these compounds, the drainages or feeder streams of Hayabuchi River were monitored. In the Hayabuchi River watershed, there was no wastewater flows, so, rain drainage water can be regarded as surface runoff water of each watershed. Water samples were collected from outlet of drainage line or that of influent to the tributary Hayabuchi on January 9, 2006. These samples represent each watershed of Hayabuchi River basin. Then, an attempt was made to assess the PFCs pollution level in each watershed and to find the characteristics of each watershed. The data of land use and population density were used as these watershed characteristics. The data of population density didn’t show any significant correlation with the concentration of PFCs. But the data of land use indicated significant correlation. The data of land use consist of 42 types, and they were transformed into area percentage in each watershed. These variables of land use, however, were correlated with each other. Thus, PCA using varimax rotation method was carried on the land use variables. Then, factor loadings (Table 1) and scores of PC1 were extracted. PC1 correlated strongly with multidwelling with shop, business distinct, commercial land, goods depot, parking and road over 22 m width in negative. So the PC1 was considered as an index for commercial and transportation land use.

Table 1 Factor loadings of land use in each principal component

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
Cropland	0.62	0.58	0.04	0.28	-0.40	0.05	0.08
Forest	0.61	-0.04	-0.15	0.19	**-0.70**	-0.10	0.08
River	0.14	-0.10	0.13	0.12	0.09	0.09	**-0.93**
Waste land	0.11	-0.20	**-0.85**	-0.38	-0.04	0.00	0.21
Dwelling with shop	0.06	0.06	**-0.91**	0.15	0.16	0.28	-0.14
Multidwelling	-0.58	-0.64	0.02	-0.15	0.04	0.15	0.22
Dwelling with shop	0.57	0.43	0.06	-0.33	0.02	0.36	-0.11
Multidwelling with shop	**-0.74**	-0.14	0.44	0.02	-0.16	0.10	0.41
Dwelling with workshop	0.03	-0.34	0.05	**0.85**	0.17	0.16	0.24
Business district	**-0.86**	-0.07	0.33	0.24	-0.06	0.12	-0.04
Commercial land	**-0.72**	0.17	0.11	-0.20	0.05	-0.04	0.61
Amusement	-0.42	-0.16	0.04	**0.72**	0.20	0.20	-0.34
Commonland	0.02	0.08	0.33	0.12	-0.06	**-0.87**	0.28
Education and welfare	0.18	-0.66	0.28	-0.05	0.42	0.02	-0.17
Goods depot	**-0.84**	0.22	-0.39	0.13	0.23	-0.13	0.05
Light manufacturing	0.01	**0.86**	0.04	-0.20	0.05	0.23	0.29
Supply equipment	-0.03	**0.81**	-0.39	-0.26	0.26	0.12	-0.06
Agricultural facilities	0.15	**0.74**	0.11	-0.26	-0.09	-0.34	-0.09
Open-space	0.30	-0.26	**0.76**	-0.15	0.34	-0.16	-0.13
Unused land	0.35	0.59	0.13	-0.48	-0.23	-0.14	-0.45
Construction	0.11	-0.03	0.05	-0.09	0.16	**-0.91**	-0.10
Parking	**-0.89**	-0.10	-0.15	0.32	0.13	0.10	0.10
Other open-space	0.02	-0.08	0.00	**-0.89**	0.15	0.26	0.23
Road over 22 m	0.28	0.67	0.19	0.22	-0.27	-0.04	0.51
Road over 12 m	**-0.83**	-0.41	-0.24	-0.16	0.05	0.12	-0.11
Road over 4 m	0.37	0.52	-0.07	0.30	0.65	-0.06	0.24
Other road	0.22	0.26	0.05	-0.17	**-0.86**	0.16	0.13

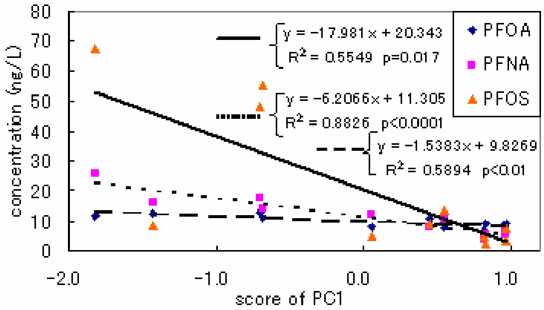

Fig. 6 Correlation between PC1 score and PFCs

The correlation between PC1 and PFCs indicated that PFOS, PFOA and PFNA were originated from commercial and transportation land use (Fig. 6). Other principal components did not show any significant correlation with any of PFCs. With these results, we concluded that PFOS, PFOA and PFNA had NPS such as commercial and/or transportation land use. It is not clear, however, which of the two land uses, commercial or transportation, was related with these congeners. Therefore, further research is necessary to explore the role of commercial or transportation land use in PFCs pollution in rivers. To the best of our knowledge, this is the first report on the role of NPS in PFC pollution.

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